

# ONE-STEP HYDROTHERMAL SYNTHESIS OF CARBON-COATED PbTe NANOWIRES FOR THERMOELECTRIC APPLICATIONS

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**Abstract.** Carbon-coated PbTe nanowires were successfully synthesized via a one-step hydrothermal process using ascorbic acid as a reducing agent and carbonization source. The average diameter of PbTe core nanowires and thickness of carbon sheaths are about 25 and 8 nm, respectively. Sequential mechanism for the phase formation, shape evolution, and carbon sheath formation was also investigated. Te nanowires were initially grown and then amorphous carbon sheaths were formed on the surface of the grown Te nanowires. At the same time,  $Pb^{2+}$  ions diffused into the carbon sheaths and react with Te nanowire, resulting in the formation of carbon-coated PbTe nanowires. Additionally, the size and shape of the PbTe nanowires were found to be determined during the initial stage of Te formation.

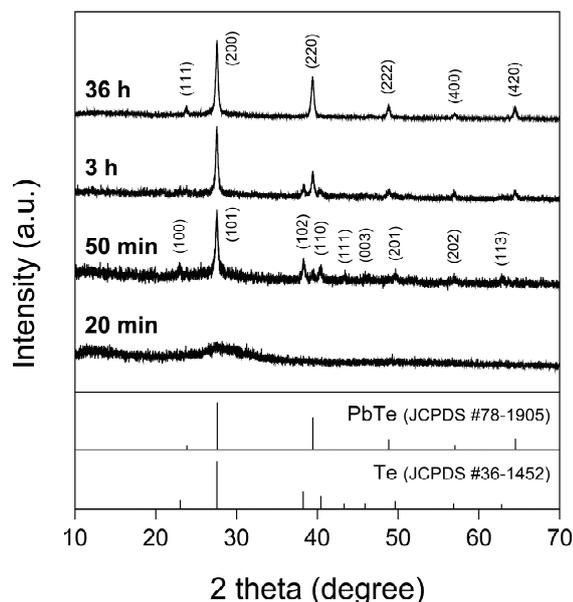
## 1. INTRODUCTION

Thermoelectric materials have potential applications in power generation, cooling, and thermal sensing [1-4]. Among the various thermoelectric materials, lead telluride (PbTe) has been identified as an ideal material for high-performance thermoelectric devices due to its narrow band gap (0.32 eV at 300K) and large Bohr radius (~ 46 nm) possessing strong quantum confinement within a large range of size [5-8]. In particular, one-dimensional (1D) PbTe nanostructures have attracted considerable interest for their potential applications in high-performance thermoelectric device construction. Tai *et al.* [5,6] and Yan *et al.* [9] reported that the thin film sample composed of the PbTe nanowires has higher Seebeck coefficient than that of the state-of-the-art bulk PbTe. However, their potential drawbacks, such as the adsorption of unwanted species (e.g., water and oxygen) on the nanowire surface as well as the unnecessary charge injection into PbTe nanowires,

could negatively affect device characteristics or stability [10-12]. Recent investigations of the nanowires with insulating sheaths have suggested potential solutions to these limitations. Xi *et al.* [10] reported the preparation of metal telluride/carbon nanocables using a hydrothermal method, with the pre-synthesized Te/carbon nanocables as templates. Liang *et al.* [11] fabricated a coaxial silica shell on the surface of PbTe nanowires via the hydrolysis of tetraethyl orthosilicate (TEOS). However, further studies on the formation mechanism of the nanowires with insulating sheaths are essential to optimize their geometry and other key characteristics.

In the present work, we report a facile one-step hydrothermal process for the preparation of amorphous carbon-coated PbTe nanowires. Ascorbic acid was used as a reducing agent and carbonization source. The sequential mechanism for phase formation, shape evolution, and carbon sheath coating of the PbTe nanowires was also studied by de-

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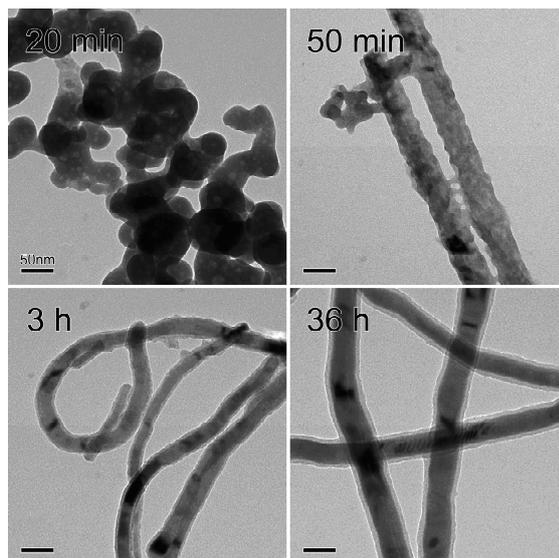
**Fig. 1.** XRD patterns of the products hydrothermally reacted at 180 °C for 20, 50 minutes, 3, and 36 hours.

tailed analysis of reaction times from the experimental data.

## 2. EXPERIMENTAL

14.2 mmol of ascorbic acid ( $C_6H_8O_6$ ) was put into a 100 mL Teflon-lined stainless steel autoclave and dissolved in 40 mL of deionized water under mild magnetic stirring at room temperature. In the next step, 0.823 mmol of cetyltrimethylammonium bromide (CTAB), 1.88 mmol of  $Na_2TeO_3$  and 1.88 mmol of  $Pb(NO_3)_2$  were added to the above solution in order; a white  $TeO_2$  was precipitated immediately upon the addition of the  $Na_2TeO_3$ . Finally, the autoclave was filled with deionized water up to 80% of the total volume, sealed and maintained at 180 °C for various reaction times (20, 50 minutes, 3, 6, and 36 hours) in a preheated electric oven, then allowed to cool to room temperature naturally. The black products were collected and washed repeatedly with deionized water and ethanol, then dried at 60 °C for 12 hours.

The phase of each resulting product was characterized by X-ray diffractometer (XRD, D/MAX-IIIC, Rigaku, Japan) with  $Cu K\alpha$  radiation ( $\lambda = 0.15406$  nm at 40 kV and 45 mA). The morphology and size of the products were observed by scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI Company, Netherland). To analyze the



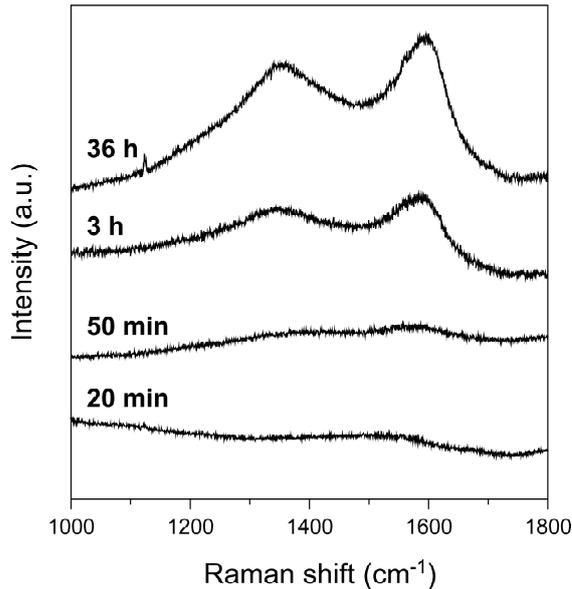
**Fig. 2.** TEM micrographs of the products hydrothermally reacted at 180 °C for 20, 50 minutes, 3, and 36 hours.

sheaths on the PbTe nanowire surfaces, Raman spectra were recorded with a high-resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon, France).

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the products synthesized at 180 °C for different reaction times (20, 50 minutes, 3, and 36 hours). The product reacted for 20 minutes is observed to exhibit an amorphous-phase. When the reaction time increased to 50 minutes, the diffraction peaks appeared. These peaks are indexed in a trigonal Te (t-Te), which agrees well with the values of literature. (JCPDS No. 36-1452). With additional increases in the reaction time, the intensity of t-Te XRD peaks decreases, whereas that the intensity of the face-centered cubic PbTe (JCPDS No. 78-1905) peaks appears and continues to increase. Particularly, the XRD pattern for the product reacted for 3 hours clearly shows a mixture of t-Te and face-centered cubic PbTe, which reflects and intermediate state of phase transition. After reaction for 36 hours, a pure-phase PbTe was ultimately obtained. The above XRD patterns confirm the phase transformation from Te to PbTe with increasing reaction time.

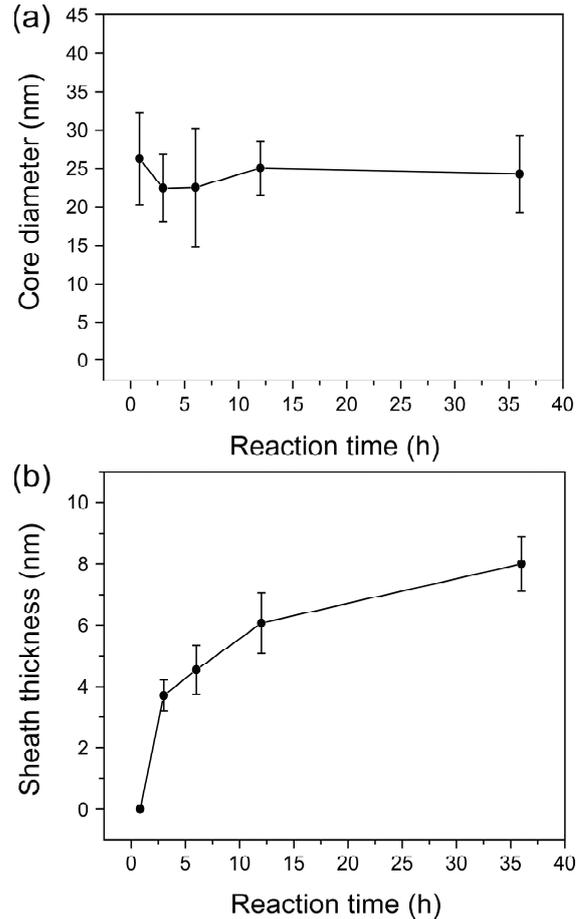
The TEM images of the products prepared at 180 °C for different reaction times (20, 50 minutes, 3, and 36 hours) are displayed in Fig. 2. These results clearly demonstrate the mechanism of the



**Fig. 3.** Raman spectra of the products hydrothermally reacted at 180 °C for 20, 50 minutes, 3, and 36 hours.

shape construction and carbon coating for the synthesized products as a function of reaction time. The amorphous products reacted for 20 minutes consist of nanoparticles with an average size of a few tens of nanometers. The t-Te products synthesized at the reaction time of 50 minutes exhibit straight nanowires with diameters of 20 – 30 nm and lengths of few micrometers. As the reaction time approaches 36 hours, the final PbTe products have greater average diameters of 35 – 45 nm and a more winding shape compared to the t-Te nanowires. Meanwhile, the obvious contrast between the inner and outer regions of the wires demonstrates a core-shell structure for the samples reacted for 3 hours and above, which shows crystalline core nanowires coated uniformly with amorphous sheaths.

Raman spectroscopy was used to analyze the composition of the amorphous sheaths, and the results are shown in Fig. 3. The resulting Raman spectra show two distinct peaks around 1346 and 1594  $\text{cm}^{-1}$  for the products reacted for 3 hours and above, which are not observed in Raman spectra of the products prepared for 20 and 50 minutes. These peaks attributed to the stretching modes of C-C bonds of the D band and G band in carbonaceous solid, respectively. The D band results from a disorder-induced band which is due to the double-resonance effect, and the G band is attributed to in-plane vibrations of graphitic carbon [13]. These results identify that the sheaths are composed of



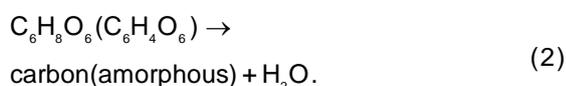
**Fig. 4.** Change in (a) diameter of core nanowires and (b) thickness of carbon sheaths as a function of the reaction time (50 minutes, 3, 6, and 36 hours) after the formation of t-Te nanowires.

amorphous carbon. The intensity of the D and G band increases in the Raman spectra as reaction time increases to 36 hours, in proportion to the increase of sheath thickness in TEM images.

The changes in core nanowire diameter and carbon sheath thickness, after the formation of t-Te nanowires as a function of reaction time (20, 50 minutes, 3, 6, and 36 hours) were investigated as shown in Fig. 4. The core nanowire diameter is maintained at 25 nm from the initial stage of t-Te formation through the completion of PbTe formation (Fig. 4a). On the other hand, the thickness of the amorphous carbon sheaths increases up to approximately 8 nm since the presence of amorphous carbon sheaths on the nanowires appeared during the intermediate stage (mixture of t-Te and PbTe) (Fig. 4b). These results suggest that the final PbTe core nanowire diameter is determined at an initial stage of t-Te nanowire formation, and that the formation of

amorphous carbon sheaths starts with the phase transition from t-Te to PbTe.

On the basis of the above experimental results, the phase and shape evolution of amorphous carbon-coated PbTe nanowires could be proposed. When the hydrothermal reaction starts, the straight t-Te nanowires are grown by the process called 'solid-solution-solid transformation'. In this process, the growth into t-Te nanowires is associated with their crystal structure. Te has the highly anisotropic inherent structure, with the basic unit being helical chains of covalently bound Te atoms, causing it to crystallize along the c-axis [14]. As the reaction proceeds, amorphous carbon is coated on the surface of the initially grown t-Te nanowires by the polymerization and carbonization of the ascorbic acid. The chemical reaction involved in this process is as follow [10,15]:



At the same time,  $\text{Pb}^{2+}$  ions diffuse into the carbon sheaths and react with Te nanowires, which results in the formation of PbTe nanowires. This reaction step is well supported by the standard electrode potentials of  $\text{Pb}^{2+}/\text{Pb}$  and  $\text{C}_6\text{H}_6\text{O}_6/\text{C}_6\text{H}_8\text{O}_6$  (-0.126 [10] and +0.06 V [16], respectively), which are evidence for the direct reaction between  $\text{Pb}^{2+}$  ions and Te nanowires without a reducing step to Pb atoms. Meanwhile, during the reaction, the straight form t-Te nanowires transform to amorphous carbon-coated PbTe nanowires with a winding shape.

#### 4. CONCLUSION

Amorphous carbon-coated PbTe nanowires were successfully synthesized through a facile one-step hydrothermal process, using ascorbic acid as a reducing agent and carbon source. The formation process of amorphous carbon-coated PbTe nanowires involves four distinctive stages: (1) the growth of straight shaped t-Te nanowires via 'solid-solution-solid transformation'; (2) induction of amorphous carbon coating on the t-Te nanowire surfaces by polymerization and carbonization of the ascorbic acid; (3) simultaneously, the diffusion of  $\text{Pb}^{2+}$  ions into the carbon sheaths; (4) the formation of carbon-coated PbTe nanowires with winding geometry by the reaction between  $\text{Pb}^{2+}$  ions and Te nanowires. The diameter of the PbTe nanowires is determined at the initial stage of t-Te nanowire formation.

#### ACKNOWLEDGEMENT

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